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1. REPORT DATE (DD-MM-YYYY) 27 Aug 1999		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To) 9/97 - 6/99	
4. TITLE AND SUBTITLE Temperature Dependence of the Cl + HN3 reaction from 300 to 480 K				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Gerald C. Manke II, Thomas L. Henshaw, Timothy J. Madden, Gordon D. Hager				5d. PROJECT NUMBER 3326	
				5e. TASK NUMBER LA	
				5f. WORK UNIT NUMBER 02	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory Directed Energy Directorate 3550 Aberdeen Ave. SE Kirtland AFB, NM 87117				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Directed Energy Directorate 3550 Aberdeen Ave. SE Kirtland AFB, NM 87117				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited					
13. SUPPLEMENTARY NOTES Chemical Physics Letters, Vol. 310, 1999, pp. 111-120					
14. ABSTRACT The rate constant for Cl + HN3 over the temperature range 300 - 480 K has been studied in a flow reactor. Based on the rate of loss of HN3 and the rate of NCl(a) generation, the temperature dependence of this reaction is described by the collision theory expression $1.2 \pm 0.3 \times 10^{-11} T^{0.5} \exp(-1514 \pm 93/T)$ , with $E(0) = 3.0 \pm 0.2$ kcal/mol or an Arrhenius fit $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.2$ kcal/mol.					
15. SUBJECT TERMS AGIL, kinetics, Cl atom reactions, HN3, hydrogen azide reactions, temperature dependent rate constants.					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  Unlimited	18. NUMBER OF PAGES  14	19a. NAME OF RESPONSIBLE PERSON Gerald C. Manke II
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) 505-853-2674

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# CHEMICAL PHYSICS LETTERS

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Chemical Physics Letters 310 (1999) 111–120

## Temperature dependence of the $\text{Cl} + \text{HN}_3$ reaction from 300 to 480 K

Gerald C. Manke II <sup>\*</sup>, Thomas L. Henshaw, Timothy J. Madden, Gordon D. Hager

*Air Force Research Laboratory, AFRL / DELC, 3550 Aberdeen Avenue SE, Kirtland AFB, NM 87117-5776, USA*

Received 10 May 1999; in final form 28 June 1999



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**Publication information:** Chemical Physics Letters (ISSN 0009-2614). For 1999, volumes 298–314 are scheduled for publication. Subscription prices are available upon request from the publisher or from the Regional Sales Office nearest you or from this journal's website (<http://www.elsevier.nl/locate/cplett>). Further information is available on this journal and other Elsevier Science products through Elsevier's website (<http://www.elsevier.nl>). Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by standard mail (surface within Europe, air delivery outside Europe). Priority rates are available upon request. Claims for missing issues must be made within six months of our publication (mailing) date.

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## Temperature dependence of the $\text{Cl} + \text{HN}_3$ reaction from 300 to 480 K

Gerald C. Manke II<sup>\*</sup>, Thomas L. Henshaw, Timothy J. Madden, Gordon D. Hager

Air Force Research Laboratory, AFRL/DELCL, 3550 Aberdeen Avenue SE, Kirtland AFB, NM 87117-5776, USA

Received 10 May 1999; in final form 28 June 1999

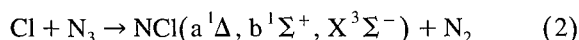
### Abstract

The rate constant for  $\text{Cl} + \text{HN}_3$  over the temperature range 300–480 K has been studied in a flow reactor. Based on the rate of loss of  $\text{HN}_3$  and the rate of  $\text{NCl}(a^1\Delta)$  generation, the temperature dependence of this reaction is described by the collision theory expression  $1.2 \pm 0.3 \times 10^{-11} T^{0.5} \exp(-1514 \pm 93/T)$ , with  $E_0 = 3.0 \pm 0.2 \text{ kcal mol}^{-1}$  or an Arrhenius fit  $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$  with  $E_a = 2.9 \pm 0.2 \text{ kcal mol}^{-1}$ . © 1999 Elsevier Science B.V. All rights reserved.

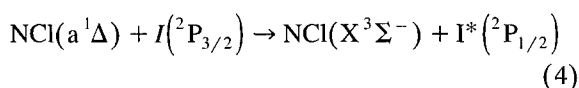
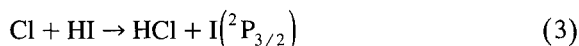
### 1. Introduction

The recent report of a direct measurement of gain [1] on the  $I(^2P_{1/2}-^2P_{3/2})$  transition in the  $\text{NCl}(a^1\Delta)/\text{I}$  chemical system has increased interest in the use of metastable nitrene halides ( $\text{NX}$ ) as energy donors for iodine-based chemical lasers analogous to the chemical oxygen iodine laser (COIL) [2,3]. There are several important advantages and disadvantages to the use of these molecules, which are isovalent with  $\text{O}_2$ . The most obvious advantage is generation of the  $(a^1\Delta)$  states in the gas phase [4–10] rather than the mixed gas/aqueous chemistry that is necessary for COIL operation. On the other hand, the  $\text{NX}(a^1\Delta)$  molecules are much more reactive than  $\text{O}_2(a^1\Delta)$  [11–13], and the scaling issues for generating high concentrations of  $\text{NCl}(a^1\Delta)$  have not yet been resolved. The  $\text{Cl}/\text{HN}_3$  chemical system

used for the generation of  $\text{NCl}(a^1\Delta)$  is summarized by reactions (1) and (2):



The  $\Delta H_0^0$  value for reaction (1) is  $-9.3 \text{ kcal mol}^{-1}$ , and the enthalpy for reaction (2) is  $-39$ ,  $-22$ , and  $-65 \text{ kcal mol}^{-1}$  for generation of the  $(a^1\Delta)$ ,  $(b^1\Sigma^+)$ , and  $(X^3\Sigma^-)$  states, respectively, using  $\Delta H_f^0(\text{NCl}) = 77.4 \text{ kcal mol}^{-1}$  [14]. The rate determining step for this process is reaction (1), which has a room temperature rate coefficient [15] of  $1.1 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Gain on the  $I(^2P_{3/2})-I(^2P_{1/2})$  transition was achieved when a small flow of HI is added to a flow of  $\text{NCl}(a^1\Delta)$ :



<sup>\*</sup> Corresponding author. Fax: +1-505-846-4807; e-mail: mankeg@plk.af.mil

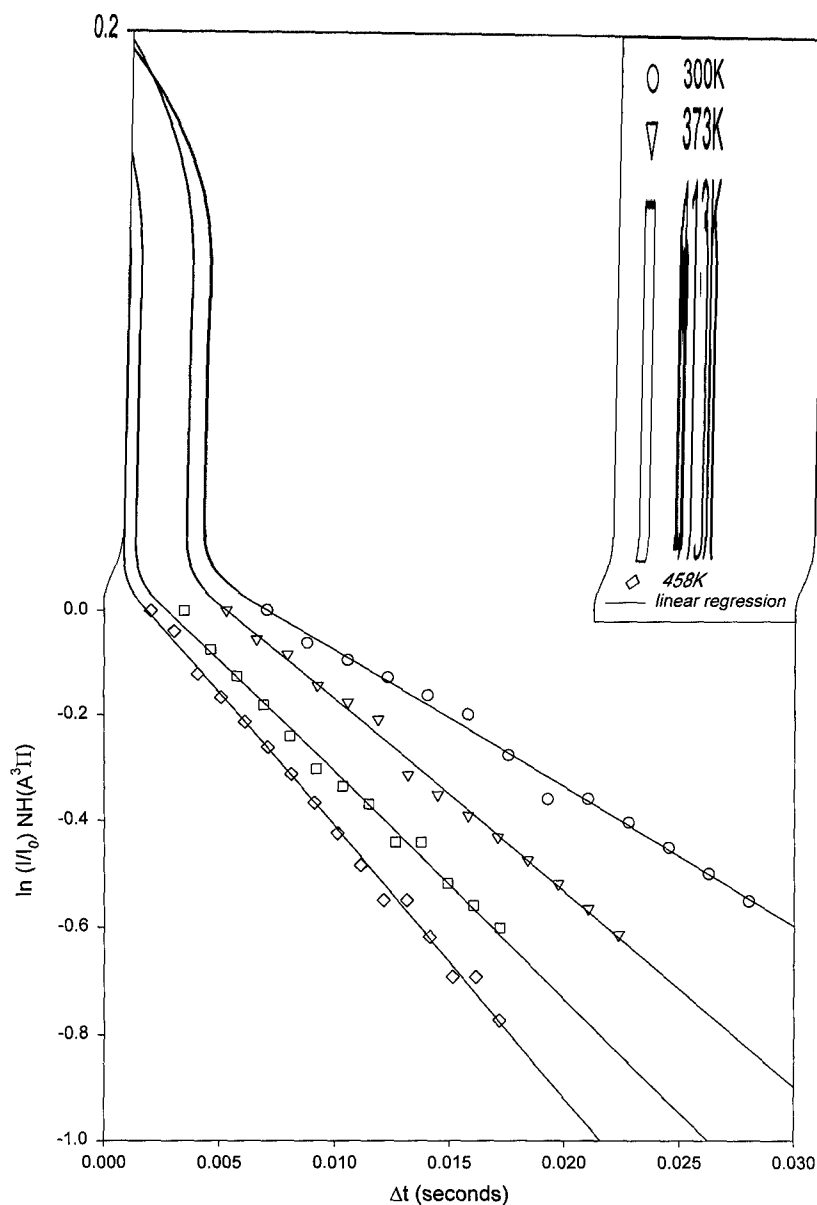


Fig. 2. Pseudo-first-order plots of  $\ln I/I_0(\text{NH}(A^3\Pi))$  versus reaction time. The experimental conditions and results are as follows: (300 K)  $[\text{Cl}] = 1.2 \times 10^{13}$ ,  $[\text{HN}_3] = 2.0 \times 10^{12} \text{ cm}^{-3}$ ,  $k = 1.4 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; (373 K)  $[\text{Cl}] = 8.0 \times 10^{12}$ ,  $[\text{HN}_3] = 3.0 \times 10^{12} \text{ cm}^{-3}$ ,  $k = 4.5 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; (413 K)  $[\text{Cl}] = 6.0 \times 10^{12}$ ,  $[\text{HN}_3] = 2.8 \times 10^{12} \text{ cm}^{-3}$ ,  $k = 6.5 \pm 0.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; (458 K)  $[\text{Cl}] = 6.0 \times 10^{12}$ ,  $[\text{HN}_3] = 1.7 \times 10^{12} \text{ cm}^{-3}$ ,  $k = 8.5 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

$\text{CF}_3\text{I}$  in 12 L bulbs. The flow rate of  $\text{HCl}$  was determined by diverting the stream to a vessel of known volume and measuring the rate of pressure rise. The bulk of the flow (typically 2.5 SLPM,  $1850 \mu\text{m s}^{-1}$ ) consisted of Ar (Airgas, UHP grade). Two microwave discharges on a  $\text{CF}_4$  (Airgas, 99.5%)/Ar mixture produced up to  $1.5 \times 10^{13} \text{ cm}^{-3}$  F atoms at 1.5 torr. Pre-prepared mixtures of  $\text{HN}_3$  and He were

stored in a stainless steel vessel.  $\text{HN}_3$  was added to the reactor via one of two sliding Pyrex injectors.

The entire reactor was encased by resistive heating units, which consisted of Nichrome wire helically wound inside a ceramic jacket. The temperature was measured by inserting several type K thermocouples into the gas stream at various points along the reactor. A flexible thermocouple was inserted

into the one of the movable injectors to provide a temperature measurement at the center of the tube. The heaters were regulated with Omega controllers (Model CN76000) with an accuracy of  $\pm 1^\circ$  at room temperature and  $\pm 7^\circ$  at 480 K. All inner surfaces were coated with PTFE, which limited the temperature to 500 K.

A 0.3 m monochromator (Instruments S.A.) dispersed the chemiluminescence collected by a short focal length lens. Two different gratings (500 or 900 nm blaze, both with 1200 grooves  $\text{mm}^{-1}$ ) were used, depending on the emission of interest. The emissions of HF ( $\Delta v = -3$ ), NF(a $^1\Delta$ ), NCl(a $^1\Delta$ ), NF(b $^1\Sigma^+$ ), and NCl(b $^1\Sigma^+$ ) were monitored with a cooled

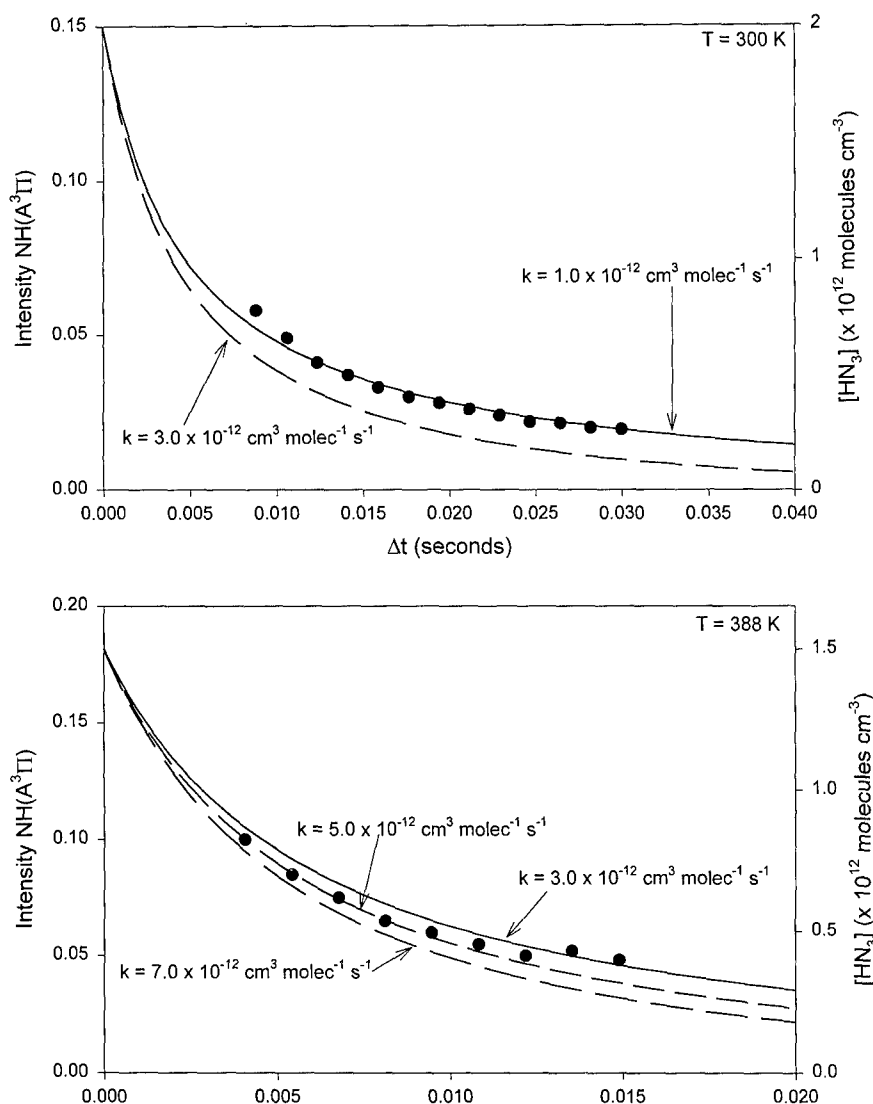


Fig. 3. Non-pseudo-first-order plots of  $I(\text{NH}(\text{A}^3\Pi))$  versus reaction time. A least-squares fitting routine was used to extract  $k_1$  from the data. The experimental conditions are as follows. Upper panel:  $T = 300 \text{ K}$ ,  $[\text{Cl}] = 1.1 \times 10^{13}$ ,  $[\text{F}] = 2.0 \times 10^{12}$ ,  $[\text{HN}_3] = 2.0 \times 10^{12} \text{ cm}^{-3}$ . Lower panel:  $T = 388 \text{ K}$ ,  $[\text{Cl}] = 6.5 \times 10^{12}$ ,  $[\text{F}] = 1.5 \times 10^{12}$ ,  $[\text{HN}_3] = 1.5 \times 10^{12} \text{ cm}^{-3}$ . Note that the data can be satisfactorily fit by several values for  $k_1$ , and the relative error for this method is large.

( $-80^{\circ}\text{C}$ ) R1767 PMT (Hamamatsu) while the UV emission from  $\text{NH}(\text{A}^3\Pi)$  was detected with a R374 PMT (Hamamatsu) cooled to  $-50^{\circ}\text{C}$ . When necessary, band pass or long pass filters were used to isolate signals of interest from unwanted background or second-order emissions. A representative spectrum (uncorrected for the relative response of the S-1

PMT) from the reaction of F and Cl atoms with  $\text{HN}_3$  is shown in the upper panel of Fig. 1.

The relative concentration of  $\text{HN}_3$  was monitored by adding  $\text{N}_2(\text{A}^3\Sigma_u^+)$  via the indicator inlet and monitoring the resultant  $\text{NH}(\text{A}^3\Pi)$  signal at 335 nm. The  $\text{N}_2(\text{A}^3\Sigma_u^+)$  molecules were generated by energy transfer from metastable  $\text{Ar}({}^3\text{P}_2, {}^3\text{P}_0)$  atoms using a

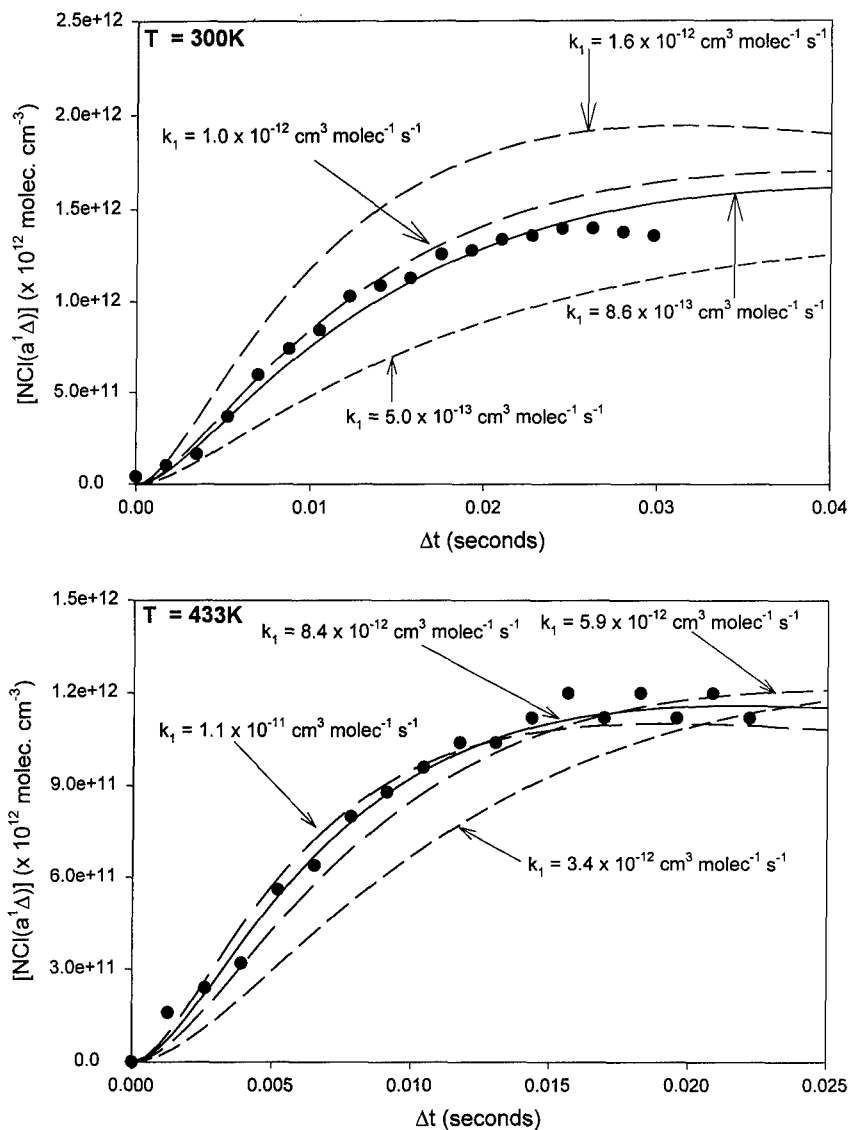


Fig. 4. Measurement of  $k_1$  via generation of  $\text{NCl}(a^1\Delta)$ . A least-squares model fit to  $[\text{NCl}(a^1\Delta)]$  versus  $\Delta t$  was used to determine  $k(\text{Cl} + \text{HN}_3)$ . The experimental conditions are as follows. Upper panel:  $T = 300 \text{ K}$ ,  $[\text{Cl}] = 1.8 \times 10^{13}$ ,  $[\text{HN}_3] = 2.0 \times 10^{13} \text{ cm}^{-3}$ . Lower panel:  $T = 433 \text{ K}$ ,  $[\text{Cl}] = 8.0 \times 10^{12}$ ,  $[\text{HN}_3] = 1.4 \times 10^{13} \text{ cm}^{-3}$ . Note that a wide range of values for  $k_1$  can satisfactorily fit the data, and the relative error for this method is large ( $\pm 30\%$ ).

rolled tantalum foil discharge design [21]. The  $\text{NH}(\text{A}^3\Pi)$  emission intensity increased linearly with the  $\text{HN}_3$  flow rate (see the lower panel of Fig. 1). With optimization of the light collection and  $\text{N}_2(\text{A}^3\Sigma_u^+)$  generator,  $[\text{HN}_3]$  as low as  $1 \times 10^{11}$  molecule  $\text{cm}^{-3}$  could be routinely detected even though the branching ratio to (5b) is low.

### 3. Results and discussion

#### 3.1. Monitoring the loss of $[\text{HN}_3]$

Under pseudo-first-order conditions ( $[\text{Cl}] \gg [\text{HN}_3]$ ) the slope of a given  $\ln(I(\text{NH}(\text{A}^3\Pi)))$  versus  $\Delta t$  plot is equal to  $k_1[\text{Cl}]$ , and the rate constant is given by simply dividing by the known  $[\text{Cl}]$ . Measurable decomposition of  $\text{HN}_3$  does not occur below 560 K and reactive loss should be the only removal process [22]. Fig. 2 shows several such measurements taken at a variety of temperatures. In each case, the initial  $[\text{Cl}]_0$  was determined by first measuring  $[\text{F}]_0$  and then adding a slight excess of HCl. The intensity decreased with time, and a regression fit to the data gives the product  $k_1[\text{Cl}]$ . At room temperature, the data is within the combined error bars of the established value for  $k_1$ ,  $1.1 \pm 0.3 \times 10^{-12}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Several measurements were performed at each temperature and Table 2 lists the average and 2 standard deviations at each temperature. The value of  $k_1$  increases up to  $1.1 \pm 0.1 \times 10^{-11}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $T = 460$  K.

Because HCl quenches  $\text{N}_2(\text{A}^3\Sigma_u^+)$  ( $k_Q = 1.3 \times 10^{-12}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [23], it was not always possible to add excess HCl and a few measurements of  $k_1$  were performed with a mix of F and Cl atoms present with  $\text{HN}_3$ . A known flow of HCl is added to a measured  $[\text{F}]_0$  and  $[\text{F}]'$  and  $[\text{Cl}]'$  calculated from the bimolecular rate law. The temporal dependence of  $[\text{HN}_3]$ , as monitored by  $I(\text{NH}(\text{A}^3\Pi))$ , is fit by the kinetic model listed in Table 1. In cases such as these, accurate measurement of  $k_1$  requires  $[\text{Cl}] \gg [\text{F}]$ , and  $[\text{F}] \leq [\text{HN}_3]_0$ . Otherwise, F removes nearly all of the  $\text{HN}_3$  and it becomes impossible to accurately extract  $k_1$  [5]. Several examples are shown in Fig. 3. In each case, the least-squares analysis produces a satisfactory fit to the data. This method, however, is inherently less sensitive than the method

described above and the error bars for  $k_1$  are significantly larger. Table 2 summarizes the  $k(T)$  data for reaction (1) based on the loss of  $[\text{HN}_3]$ .

#### 3.2. Generation of $\text{NCl}(\text{a}^1\Delta)$

The rate determining step for the generation of  $\text{NCl}(\text{a}^1\Delta)$  is reaction (1). For nearly any set of conditions where no  $[\text{F}]$  is present, the rate of  $\text{NCl}(\text{a}^1\Delta)$  growth is dependent upon  $k_1$ . Fig. 4 shows several examples of the growth of  $\text{NCl}(\text{a}^1\Delta)$  versus  $\Delta t$  at a variety of temperatures. In each case the linear least-squares fit to the data is indicated by the solid line, while alternate values for  $k_1$  are shown by broken lines. As expected, the established value for  $k_1$  is reproduced at room temperature. However, the precision of this method is quite poor. As the plot shows, several values, up to  $\pm 30\%$ , also give reasonable fits to the data. This method is also susceptible to error in other ways. For example, as  $k_1$  increases the value of  $k_2(T)$  (which was fixed to the room temperature value) becomes more important because  $\text{N}_3$  and  $\text{HN}_3$  compete for reaction with  $[\text{Cl}]$ . Most importantly, it is difficult to generate observable  $I(\text{NCl}(\text{a}^1\Delta))$  without high  $[\text{Cl}]_0$  and  $[\text{HN}_3]_0$ , which may cause additional problems with quenching. Although this method is less satisfactory for the determination of  $k_1$ , the results agree quite well with those obtained by monitoring  $I(\text{NH}(\text{A}^3\Pi))$  (see Table 3).

All of the  $k(T)$  data for reaction (1) are summarized in Tables 2 and 3 and in Fig. 5. A least-squares

Table 3  
Summary of the  $k(T)$  measurements via generation of  $\text{NCl}(\text{a}^1\Delta)$

$T$ (K)	$k(T)$ ( $\times 10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
300	$0.89 \pm 0.27$
338	$2.6 \pm 0.8$
368	$3.4 \pm 1.0$
383	$4.8 \pm 1.4$
388	$5.8 \pm 1.7$
403	$7.7 \pm 2.3$
433	$8.4 \pm 2.5$
448	$9.3 \pm 2.8$
468	$11 \pm 3$



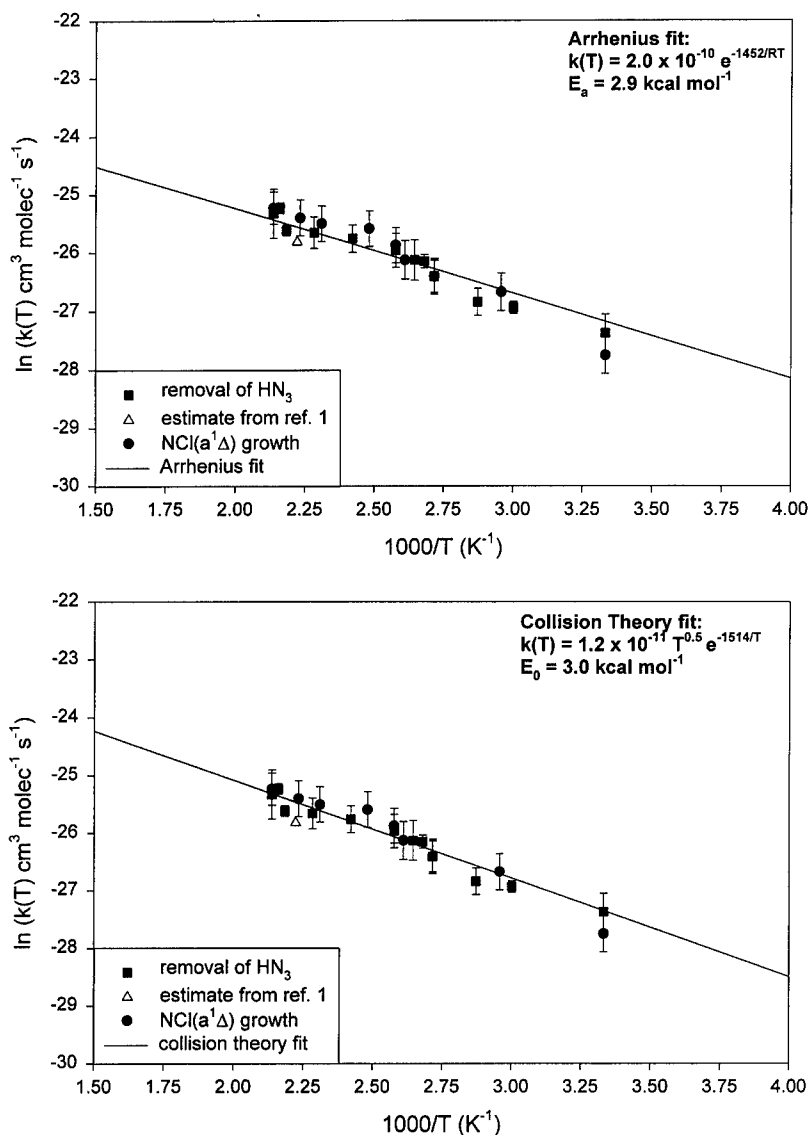


Fig. 5. Arrhenius and collision theory fits to the  $k_1(T)$  data. Upper panel: The  $k_1(T)$  data is fit by the Arrhenius expression. The best fit is achieved for  $A = 2.0 \times 10^{-10}$  and  $E_a = 2.9$  kcal mol $^{-1}$ . Lower panel: A collision theory expression is used and  $A = 1.2 \times 10^{-11}$  and  $E_0 = 3.0$  kcal mol $^{-1}$ . In both panels data from both the loss of  $\text{HN}_3$  and generation of  $\text{NCl}(a^1\Delta)$  techniques are shown.

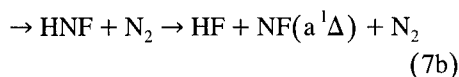
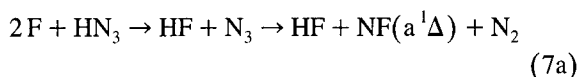
analysis of the data using the collision theory expression,  $AT^{0.5} \exp(-E_0/RT)$ , results in a satisfactory fit with  $A = 1.2 \pm 0.5 \times 10^{-11}$  and  $E_0 = 3.0 \pm 0.3$  kcal mol $^{-1}$ . The Arrhenius expression was also used to fit the data:  $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$  with  $E_a = 2.9 \pm 0.3$  kcal mol $^{-1}$ . The data in Fig. 5 also includes an estimate for  $k_1$  calculated

from the data reported in Ref. [1], and excellent agreement is achieved.

#### 4. Discussion

While several azide/atom (F, Cl, and H) reactions have been characterized at room temperature,

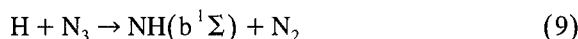
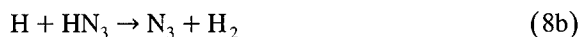
there have been few measurements for  $T > 300$  K. For example, reaction (7)



is known to be an efficient source of the  $\text{N}_3$  and  $\text{NF}(\text{a}^1\Delta)$  radicals. The room temperature rate constant [5] for (7a) is established as  $1.1 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the nascent HF vibrational distribution from reaction (7a) is 0.36:0.36:0.22:0.06 for  $v = 1-4$ . Microscopic branching between direct abstraction and addition–elimination channels may account for the rather flat vibrational distribution. The branching to HNF (7b) has been established [24] as  $0.03^{+0.02}_{-0.001}$ . The rate coefficient for the reaction of H atoms with  $\text{HN}_3$  has been measured [25] from 300 to 460 K and  $k(T) = 2.5 \times 10^{-11} \exp(-2315/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The reaction produces  $\text{NH}_2(^2\text{A}_1, \nu_2 \leq 20)$  [26] and minor amounts of  $\text{NH}(\text{A}^3\Pi)$  and  $\text{NH}(\text{b}^1\Sigma)$ .



The mechanisms for  $\text{NH}(\text{A}^3\Pi)$  and  $\text{NH}(\text{b}^1\Sigma)$  production are not well established, but they are presumed to be generated by secondary reactions such as [26]:



Prior to this report, the only halogen/azide reaction that had been characterized  $T > 300$  K was  $\text{Cl} + \text{ClN}_3$ :



Combourieu et al. used mass spectrometric detection to measure the temperature-dependent rate constant between 300 and 657 K [27]. They reported a moderate temperature dependence of  $k(T) = 2.3 \times 10^{-11} \exp(-554/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The present results indicate a moderate temperature dependence for the reaction of  $\text{Cl} + \text{HN}_3$ , with  $E_a \approx 3 \text{ kcal mol}^{-1}$ . The pre-exponential factor is large

and requires some comment. Hydrogen atom abstraction reactions such as  $\text{F} + \text{HCl}$  ( $k = 4.4 \pm 1.5 \times 10^{-11} \exp(-400 \pm 100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [28] and  $\text{Cl} + \text{HBr}$  ( $k = 4.8 \times 10^{-11} \exp(-454/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [29] have A factors which are  $\sim 2-3$  smaller than the present result. Halogen atom addition reactions, on the other hand, typically have much larger pre-exponential factors. For example, a relevant comparison may be made with the fast reaction  $\text{F} + \text{HN}_3$ ,  $A \geq k_{300} = 1.1 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Chlorine atoms are known to add to olefins (e.g.,  $\text{C}_2\text{H}_4$  [30],  $\text{C}_2\text{H}_3\text{Br}$  [31], and  $\text{C}_2\text{H}_3\text{Cl}$  [32]) and these reactions are very fast at room temperature,  $k(300) = 1.5 \pm 0.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The  $\text{Cl} + \text{olefin}$  reactions also have very small activation energies, probably on the order of a few hundred  $\text{cal mol}^{-1}$ . For example, assuming  $E_a = 0.3 \text{ kcal mol}^{-1}$ , and using  $k_{298}(\text{Cl} + \text{C}_2\text{H}_3\text{Br}) = 1.43 \pm 0.29 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the A factor is  $2.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Clearly, the large pre-exponential factor for  $\text{Cl} + \text{HN}_3$  is consistent (i.e., within a factor of 2–3) with other Cl atom reactions and is suggestive of a Cl atom addition reaction rather than hydrogen abstraction.

The main products for reaction (1) are assumed to be  $\text{HCl}$  and  $\text{N}_3$  even though vibrationally excited  $\text{HCl}$  has not been observed (only  $\text{HCl}(v=1)$  is energetically possible) and the generation of  $\text{HNCl}$  cannot be ruled out. Independent confirmation of this could be accomplished in one of several ways: laser-induced fluorescence detection of  $\text{N}_3$  or infrared absorption of  $\text{HCl}(v=0,1)$  generated by reaction (1) are the most easily implemented. Virtually nothing is known about the species  $\text{HNCl}$ . If one assumes that  $\text{Cl} + \text{HNCl}$  is sufficiently exothermic to give  $\text{NCl}(\text{a}^1\Delta)$ , by analogy to the  $\text{F} + \text{HN}_3$  system, both  $\text{N}_3$  and  $\text{HNCl}$  should react rapidly with Cl atoms to give  $\text{NCl}(\text{a}^1\Delta)$ .

## 5. Conclusions

The temperature dependence of the reaction  $\text{Cl} + \text{HN}_3$  has been measured in a heated flow reactor. The rate coefficient was measured by monitoring the loss of  $\text{HN}_3$  and the rate of generation of  $\text{NCl}(\text{a}^1\Delta)$  versus time for known starting concentrations. The

rate constant data was fit by an Arrhenius expression of  $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$  with  $E_a = 2.9 \pm 0.3 \text{ kcal mol}^{-1}$ . A collision theory fit to the data gave the expression  $1.2 \pm 0.5 \times 10^{-11} T^{0.5} \exp(-1514 \pm 150/T)$ , with  $E_0 = 3.0 \pm 0.3 \text{ kcal mol}^{-1}$ .

## Acknowledgements

The US Air Force Office of Scientific Research supported this work. G.C.M. also wishes to acknowledge the National Research Council for support. The authors are grateful for helpful discussions with Prof. R.D. Coombe, Prof. M.C. Heaven, and Prof. D.W. Setser.

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